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(a) Energy polymerizable composition containing organometallic initiators.

(3) An energy polymerizable composition and process therefore, comprising a cationically polymerizable material and a catalytic thy effective amount of an ionic selt of an organometallic complex cation as polymerization initiator, said ionic selt of an organometallic complex cation being capable of adding an intermediate strength nucleophile or upon photolysis capable of liberating at least one coordination site, said inetal in said organometallic complex cation being selected from elements of Periodic Groups IVB, VB, VIB, and VIIB are disclosed Certain of the organometallic metallic polymerization initiators are novel cationic salts.

Description

Energy Polymerizable Compositions Containing Organometallic Initiators

CONCESSION OF SERVICE

Technical Field

The present invention relates to a process for the polymerisation of cationically-sensitive meterials employing as polymerization initiator a certain class of ionic organometallic compounds. In another aspect, it relates to polymerisable compositions containing cationically-sonsitive materials and organometallic complex compounds. In a further aspect, it relates to certain organometallic polymerisation initiators.

Background Art

the above-mentioned patents teaches the acceleration of the and carboxylic acids, and U.S. Patent No. 4,237,242 relates further known that a metallocene, such as ferrocene, can be discloses the use of bis- and tris-salicylic soid complexes The prior art describes various processes for the of thromium(III) to catalyze the reaction between epoxides acid group-containing polymers with polyepoxides. Each of manganese, iron, etc.) of acetylacetonate type ligands to accelerate the thermally initiated reaction of carboxylic basic amhydrides, organic peroxides, and quinone. It is described in U.S. Patent No. 3,705,129. U.S. Patent Nos. ambydrides or polymercaptans. U.S. Patent No. 3,867,354 polymerization of apoxy materials. It is known to cure epoxy materials by use of curing additives such as polyreaction between polyepoxides and polyfunctional curing initiation of c. tionic polymeritation, particularly the used as a curing accelerator for spony materials and is 3,709,861 and 3,714,006 describe the use of cyclopentadienylaanganese tricarbonyl for the acceleration of the light-catalyzed reaction between polyepoxides and acid additives, but they do not teach the polymerization of to the use of transition metal complexes (chromium,

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spoulds group-containing compositions not containing a curing additive.

The polymerization of cationically-polymerizable materials, specifically spoulds group-containing meterials, in the absence of curing additives is, however, well known. Among such processes are those in which the polymerization catalyst (also called sensitiser or initiator) is (1) a radiation-sensitive only sait of a Lawis acid (e.g. dissonly saits as are described in U.S. Petent No.

10 3,794,576 and U.S. Patent No. 4,080,274; balonium salts so are disclosed in U.S. Patent No. 4,026,703; and the onlum salts of Group VIA elements, particularly the salfonium salts, as are disclosed in U.S. Patent No. 4,026,600); (2) a discrbonyl chelate compound of a Group IIII-WA element is disclosed in U.S. Patent No. 4,086,891; (3) a allume salt which is used for the polymerization of tetrahydrofura as is described by Moodhouse, et al. 1, No. Chem. Soc. 100, 996 (1978); and (4) titamoceme dichloride which

is used for the polymerization of epichlorohydrin and 2-chloroethylvinyl either as is described by Kaszijams et al., 3. Polym, Edii, Chem. Ed. 10, 2013 (1972) and 1bid. 14, 3547 (1976). Compositions containing the aboms—mentioned catalysts are unsatisfactory "scause vitigut the addition of optical sensitients they are limited to ultresiolet redistion for palymeriation. Purphermore, the dicarbomyl chulatem and moisture sensitive

Disclosure of the Invention

and dichloribe requires a co-catalyst.

and the titeno

The present invention provides a pracess for the polymerisation of cationically-sensitive materials of utilizing as catalyst a cationic compound which is a selt of prognometallic complex cation. By selection of the metal and ligands in the organometallic complex and the counterion used, the relative thermal stability and wave-langth of sensitivity (from 200 to 600 nm) can be adapted

for various applications.

In accordance, with the present invention there re provided energy-curable compositions comprising:

- el a cationically-polymerizable meterial and
- Periodic Groups IVB, VB, VIB, VIIB, and VIIIB. a catalytically-effective amount of an ionic phenylphosphine or upon photolysis capable of liberating at least one coordination site, said metal of said organometallic complex sufficient to effect polymerization, said mediate strength nucleophile such as trisalt of an organometallic complex cation cation being capable of adding an interionic salt of an organometallic complex cation being selected from elements of
- 15. There is also provided a process for the polymerization of cationically sensitive material comprising the steps of:
 - with a catalytically-effective amount of the cation, thereby forming a mixture, and mining the cationically-sensitive material ionic salt of an organometallic complex
- allowing the mixture to polymerise or adding energy to the mixture to effect polymerization thereof.

As used in this applications.

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cationically-polymerizable material at least to a degree to "catalytically effective amount" means quantity sufficient to effect polymerization of the increase the viscosity of the compusition, and

"intormediate strength nucleophile" means a. chloride, e.g., trialkyl- and triarylphosphines, trialkylnucleaphile intermediate in strength between hydride and and triarylphosphitos, pyridimes, and anilines.

Detailed Description of the Invention

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cations useful in the compositions and processes of the The ionic salts of the organometallic complex invention are compounds having the formula:

2x 24(97)(57)(17) (12)(1627)(1627)(1617) wherein Me, MD, MC, and Md represent metal atoms which may ments of Periodic Groups IVB, VB, VIB, VIIB, and be the same or different selected from the ele-

nuclear, binuclear, triauclear, or tetranuclear complex with the provise that Pormula I can represent a monocompound comprising No. 1881b, 1881bit, or 1888 New respectively with their attendent ligands, Li

each capable of contributing two to twelve T-electrons unsubstituted acyclic and cyclic unseturated comprund each Lle, Llb, Llc, and Lld represents none, or 1, 2, or 3 ligands centributing P-electrons that can be the same cyclic arquetic and heterocyclic arometic compounds. and groups and substituted and wesubstituted carboor different ligand selected from substituted and to the valence shall of He, He, Me, and He, respectively:

ri-dentate ligands, each donating 2, 4, or 6 a the same or different selected from mono-0-electrons to the welence shall of Me, Mb, MC, and tributing an even number of 0-electrons 12c, and 1.2d represents none, or 1 to 6 Hd, respectively: L20, L20, ligende a that can di-. and

valence abell of Me, MP, MC, and Md, respectively? eath Lis, Lib, Lic, and Lid represents none, 1, or 2 ligands contributing one 0-electron each to the

*-electrons to the valence shells of two or more metal represents none, or 1 to 6 bridging ligands containing o-electrons that can be the same or different ligand and cyclic unsaturated compounds and groups and subselected from subotituted and unsubstituted acyclic stituted and unsubstituted carbocyclic aromatic and acting as a bridging ligand contributing 2 to 24 heterocyclic aromatic compounds, each capable of atoms Mª, Mb, MC, or Md simultaneously;

represents none, or 1 to 12 bridging ligands contributing an even number of 0-electrons that can be the same or valence shells of two or more metal atoms Mª, Mb, MC, different selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 g-electrons to the or me simultaneously; 10 L5

1, 2, 3, or 4 d-electrons to the valence shells of two represents mone or 1 to 12 bridging ligands contributing or more anstal atoms Na, Nb, NC, or Nd simultaneously? with the provise that the total electronic charge con-

and Le plus the sum of lonic charge on Me, Mb, Mc, and Md [34, 130, 125, 135, 13c, 12c, 13c, 13d, 12d, 13d, 14, 15, 20 tributed to We, Mb, WC, and Md by the ligards Lie, Lie, results in a residual set positive charge of e to the

is an integer having a value of 1, 2, or 3, the residual x is a halogen-containing complex anion of a metal or electrical charge of the complex cations complex

f is an integer of 1 to 3, the number of complex anloss metalloid:

required to neutralize the charge e on the complex Cation; and

g, h, j, and h independently are 0 or 1, with at least one in a preferred composition of the invention, the of thes being equal to 1.

salts of the organometallic cation have the formula:

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wherein

of represents a metal selected from elements of the Periodic Groups IVB, VB, VIB, VIIB, and VIIIB;

selected from the same group of ligands from which $\mathbb{C}^{k_{\Phi}},$ w-electrons that can be the same or different ligand represents none or 1 to 6 ligands contributing an even ligands from which Lia, Lib, Lic, and Lid ligands of Llb, Lic, and Lld ligands of Pormula I is selected? L' represents none, one or two ligands contributing different ligand selected from the sums group of number of o-electrons that can be the same or Formula I is selected;

buted to He by L? and LB plue the lonic charge on He results e, f, and X have the same definition as given in Pormula I. In a most preferred composition of the invention. in a residual net positive charge of e to the complex; and with the provise that the total electronic charge contrithe salts of the organometallic cation are movel and have the formula:

111 ((L9) (L10) 100) *qr,

where in

HP represents a metal selected from Ct. Mb. M. Hm. No. Po. 8

n⁶-benzene compounds and gompounds having 2 to 4 fused rings each capable of contributing 3 to 8 "-electrons L' represents 1 or 2 ligands contributing v-electrons that substituted and unsubstituted n3-allyl, n3-cyclopents compounds swlegged from 16-benzene and substituted can be the samp or different ligand selected from . clenyl, and n7-cycloheptatrienyl and n6-aromatic to the valence shell of MP:

represents none or 1 to 3 ligends contributing an even different ligand selected from carbon monoxide or number of o-elegtrons that can be the same of

buted to all by L⁰ and L¹⁰ plus the ionic charge on metal AP atts to a met routined positive charge of q to the conwith the grantes that the total electrolic charge coatri-

- to an image boding a value of 1 or 2, the residual per-centaining complex salon selected from electrical charge of the complex cations per - meg out they and
- mired to sestralise the charge q on to an analyse haring a value of 1 or 2, the numbers of
- L. II. and III are authories consitive in addition to being stallic cetions having formulas THE All sensition.
 - All Marmes Lie to 1.10 are usli know in the art team estal espannetallic compounds.

tetraceme, and substituted and unsubstituted carbocyclic

n3-cyclobezadienyl, "#-cyclobeptatriens, "#-cycloocta-

as actgarate, -Emb. group, acetyleate, -CHC- group tannes the, the, the, east the in Permits Is and male II. are growided by any measurerie or polywis beriefer as excessible esecurated group. matic (presp tables have ecceptable e-cleatrons maler unique of the com constitle", it to ment that the compound for des at the cased and 512

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pound, it is manic, as emplaised bolow, that the ligard con enflictementy chans up a antel atom to focus a 4-bond joining the wasserented graup to the notal atom. By polymeric comlivisible fitte way fine perticles of high earliess are so stact, a.g., cettifydiathetas atc, or that the empound is ses e indensitate e.e., trichlerethylens: se allene. seie bydracistes, e.g., enterles as that the anististical graup (facinting prometic graup) to A cetyl toccase as acces, e.g., any as bearing the emercement group is colubbe in a tion andian, outh as in elicited, e.g., methanols a of free shich the accessible compound to december on an

having less than 60 carbon atoms, and up to 10 hetero atoms discetylens, butadiess, 1,2-dimethylacetylens, cyclobutens, acetylese, propylene, methylecetylene, 1-butene, 2-butene, Illustrative of ligands Lie, Lib, Lic, Lid, and compounds having less than 100 carbon atoms, preferably armenic, selenium, boron, antimony, tellurium, silicon, heptene, 1-octene, 4-octene, 3,4-dimethyl-3-herene, and peatene, cyclopeatese, bexene, cyclobeaese, 1,3-cycloheradiese, cyclopentadiese, 1,4-cycloberadiese, cyclo-L' are the linear and cyclic olefinic and acetylenic permentum, and tim, such as, for example, ethylene, selected from nitrogen, sulfur, oxygen, phosphorus, 1-decemes n3-allyl, n3-pentenyl, norbornadiene. and beterocyclic arquetic ligands having up to 25 rings and beasene, 16-2, 4, 6-triphenylphosphehenzene, n5-selenophene, suitable growstic compounds can be found by consulting any n6-triphamylene, n6-milabenseme, n6-arsabensene, n6-stibaup to 100 carbon atoms and up to 10 hetero atoms selected n6-dibensestannepint, n5-tellusephene, n6-phenothiarsine, selenium, boron, antimony, tellurium, silicon, germenium, n6-selenemthrene, n6-phenoxaphospaine, n6-phenarsanine, n6-phenatelluratine, and n6-1-phenylborabensene. Other nf-glucress, nf-asphibalens, nf-esthracess, nf-chrysens nl2-paragelophame, ml2-1,4-diphenylbutame, m3-pyrrole, né-bearozasine, né-Maole, né-acridine, né-carbazole, nf-pyrame, n7-cyclohaptatriesyl, n6-triphenylmethens, from nitrogen, sulfe, oxygen, phosphorus, arsenic, and in, such as, for example, "5-cyclopentadienyl, n3-thiophene, n3-fuths, n6-pyridine, n6-y-picoline, qé-benzene, né-mesitglese, né-bezzenthylbensene, na-quinaldine, ne-benzopyren, ne-thiochrone, of many chemical handbooks.

As mentioned before, the ligand can be a unit of a polymer, for example the phenyl group in polystyrene, poly(styrem-cobutations), poly(styren-comethy) meth-

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polymethylehenyleilonene; the cyclopentadiene group in polymethylehenyleilonene; the cyclopentadiene group in palytrinylongiantadiene), polytu⁴-cyclopentadiene); the perialise group in polytrinyleyridise), etc. Polymers perialise estate overage molecular weight up to 1,000,000 or mere can be estat. It is preferable that 5 to 50 percent of the essentiated or ecumetic groupe present in the polymer.

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henyletibles trimethylgermans tributylcan be enterticated by groups that do not interfere with th. ch as methylmoscapto (thismathony), phonylmercapto contyle and beneath; byterocarbylearbonyleny such as any, and eyelebenesseesthonylony; hydrocarbyl-1. bears, dedacyl, tetracosasyl; phosyl, bentyl, allyl include hydrocarbyl groups such as methyl, 144, o.g., oceanide, tensenidos anos boryls belo. estenden, entinosy, tellurius, silicon, permenius no the embeddity of the ligand to the extent that my, betany, and phonony; hydrocarbylasrcapto men of the ligands tle, tlb, tlc, tld, and t? peachonyl: hydrocarbylcarbonyl such as ciang of the Meand with the metal atom or which do mil. and ethymyls hydrocarbylony groups ies of embettenting groups, all of which preferably Less then 30 carbon atoms and up to 10 hetero atoms The lasts, brune, and fluore, bydroug; eyano; chylosycachosyl such as methosyto, and directly landace diphosylphosphine, and ridge anch as being, cyclopeatas amphibo, is tias methylacianss ethyltolluros and trimethylsilotys ming with the metal atom does not take place. ted free attrages, sulfur, ouyges, phosphorus, alens elen

Liginate 120, 120, 12c, and 12d in Formule 1, and 10 in Formule 11 and provided by monodestate and polydenter. Compounds prefetably containing up to about 10 carbon atoms and up to 10 kespero atoms selected from altrogen,

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methylidene, ethylidene; suitable polydentate compounds or compounds of Group VA elements such as amonia, phosphine sulfur, oxygen, phosphorus, arsenic, selenium, antimony, compounds preferably forming with the metal, Mª, M^b, M^c, and tellurium, in addition to the metal atom, following tributylphosphite, isonitriles such as phenylisunitrile unsaturated ring. Examples of suitable monodentate com-1,2-bis(diphenylarsino)ethans, bis(diphenylphosphino)ethanol, butanol, and phenols nitro-cuium (1.e., NO*): triphenylphosphine, triphenylarsine, triphenylatibine, butyliscaitrile; carbene groups such as ethoxymethylpounds or groups are carbon monoxide, carbon sulfide, carbon selenide, carbon telluride, alcohole such as loss of sero, one, or two hydrogens, the polydentate carbene, dithiomethoxycarbane; alkylidemes such as trimethylamine, trimethylphosphine, triphenylamine, Hd, and HM, a 4-, 5-, or 6-membered saturated or groups include 1,2-bis(diphenylphosphino)ethane, methans, ethylenediamine, propylenediamine,

oxime. Other suitable groups are the inorganic groups such hydridotripyrazolylborate; the hydroxycarboxylic acids such se 2.4-pentanediones hydroxyhetones such as 2-hydroxyacetobis(perfluoromethyl)-1,2-dithiolene: aminocarboxylic acids phenones a-hydroxygmines such as salicyladoxine; hetoxines se glycollic acid, lactic acid, salicylic acid; polyhydric bouylic diemides such as oxalemide, biuret; direcones such se, for example, CBT, SCHT, PT, OHT, ('1", Br . I', and HT such as benail oxime; and glycaimes such as dimethylglysuch as alanine, glycine and oraninobennoic acids dicarr carbamte, dibensyldithiocarbamete: xanthates such as et hydroxyamines such as ethanolamine, propanolamine, and and the organic grifups such as, for enample, acctoay, ly, etc. As mentioned before, the phenols such as catechol and 2,2'-dihydromybiphenyl; 2-aminophenol; dithiocarbemetes such as diethyldithiomanthate, phenyl manthater the dithiolenes such as diethylemetriamine, 1;3-diisocyanatopropame, and formylong, benzuyle

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Suitable redicals 1.9, 1.9c, and 1.3d in formule I include any group baving in its etructure an atom with an emakered electron. Suitable groups can contain any cantes atoms and betare atoms but preferably contain here then 30 carbon atoms and up to 10 betare atoms

enlacted from editions, selfer, caryon, phosphorus, accorde, selection, selfers, tellurium, silicon, germanium, tim, and bearm. Essapins of such groups are hydrocathyl groups each as mathyl, other, propyl, haryl, dodecyl, phospi, calgri, cit.; manaturated hydrocathyl groups such as cient, aligh, brisnyl, quickensnyl; the hydrocathyl derivations of George IV alconer, ouch as trianthylgermanium, crishmayltin, and trianthylallyl, etc.; and organic groups

ment as family, acatyl, propionyl, acryloyl, octadecoyl, semmyl, calescentifonyl, emalyl, malonyl, orphthaloyl. thend to become I to provided by any emantic or polyments companie having an accessible emantical grant, and as an acetylasic, -CEC- group or

enganties of the total melecular weight of the compound.
Illestrative of lighed L⁴ are the linear and

equite diese and eccylanic compounds professibly having has then for contact occanasis professibly having has then for contact occanasis, and up to 10 hetero atoms and expension, subfact, only on the second stans and the contact, and the contact, and the contact, and the contact and 1.3-cyclobeardisms, o'-lift, o'-percentisms, professions, and 1.4-cyclobeardisms, o'-lift, o'-percentisms, o'-cyclobeardisms, o'-cyclobeardi

ne-arasbenzene, nedatibabensame, ne-2,4,6-triphenylphosphabensene, n3-selencimene, n6-dibenzostannepine, n5-telluron6-1-phenylborabengone. Other suitable aromatic cumpounds can be found by consulting any of many chemical handbooks. and up to 10 hetero atoms selected from nitrugen, sulfur, (7,8,9,10,10a,10b)chrysene, n6-triphenylene, n6,n6'-perané-bengopyran, né-thiochrome, né-benzomazine, né-indole, phene, n6-phenothigraine, n6-selenanthrene, n6-phenoxaexample, n5-cyclopentadienyl, n6-benzene, n6-mesitylene. oxygen, phosphorus, ersenic, selenium, boron, antimony, trienyl, "F-triphenylmethame, n5-pyrrole, n5-thiophene cyclophane, n6, n6'-1,4-diphenylbutane, n6-silabenzene, tellurium, silicon, germanium, and tin, such as, for n6-anthracene, n6-chrysene, n6-pyrene n7-cycloheptaphosphine, n6-phendrazine, n6-phenatellurazine, and n5-furan, n6-pyridine, n6- -picoline, n6-quinaldine, n6-hoxamethylbenzene, n6-fluorene, n6-naphthalene, n6-acridine; n6-carbazole, n8-(1,2,3,4,4a,12a)-n6-

solubility of the figand to the extent that complexing with such as methylmerempto (thismethoxy), phenylmercapto (thioacetony, benzoxy, and cyclobenenecarbonyloxy; hydrocarbyldodecyl, tetracoschyl, phemyl, benzyl, allyl, benzylidene. the metal atom dost not take place. Examples of substituting groups, all of which preferably have less than 30 phenoxy); hydrocathyloxycathenyl such as methoxycarbonyl of phenomy: hydrocarbylmercapto groups and phenoxycarbonyl: hydrocarbylcaruonyl such as formyl, antimony, tellurium, silicon, germanium, tin, and boron, include hydrocarbys groups buch as methyl, ethyl, butyl, mitrogen, sulfur, emygen, phosphorus, arsenic, selenium, groups that do not interiers with the complexing of the Each of the ligands L can be substituted by ligand with the megal atom or which do not reduce the carbon atoms and up to 10 betero atoms selected from acetyl, and benzogl: hydrogarbylcarbonylosy such as ethenyl, and ethyaple hydroserbyloxy groups such as mathony, butony.

gerbonemido, e.g., ecetamido, benzamido: azur buryli halo,

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e.g.. chloro, iodo, bromo, and fluoro, hydrony; cyamo; nitro; mitroso, cmo; dimethylamino; diphenylphosphimo, diphenylarateo; diphenylatibimo; trimethylparmana; tributyltim; methylmellemo; ethyltalluro; and trimethylmiloxy; comdensed timps much on benzo, cyclopenta; neghtho, indemo; and the like.

eposebenylie deign each as glycollic seid, leetle seid, atems and up to 10 hetero etems selected from altrogen, sel-1.3-411sequentagenphes, and hydridetripyresolylbecate; the engiliementerile; suitable polydentate compounds or Ligard L⁵ is provided by monodentate and polyden-1.2'-dibytominitation in the contraction of other contraction, tate compounds preferably containing up to about 30 carbon disectores and as 2.4-perioandieses hydroxytetones such as phenol: dithiocerbentes such as itethyldithiorethenets, dibinayldithiotethmate; mentheten doctions techniques duch as density extent and glyoxines such gaste groups such as, for example, Or", SOT", F", OH", C1" old and phonelly mitrosonium (1.e., 80°); compounds of as disethylglycular. Other suitable groups are the inorhime, trimbanylarsime, trippenylatibine, iscaltriles bouyild solds such as alsolde, glycine and o-maincheagoic m taclade 1,3-tistetphonylphosphinolethene, 1,2-bisher, onygen, phosphorus, eroento, selentum, estimony, an trees 4-hydronyonides ouch as salleylasuch as other sanchete, giving l'amthates the dithiolones mole such as catachal and ch as historellecementy1)-1,2-dithisless animearscids dicerborylie dismides such as orelanide, bluret, infloredientes, proppiesedientes, dicthylesetrientes, Wlereins bethang, bis (diphenylphosphino)as these, . W. elements Outh as tripbonylemiss, tripbonyl-Menido, estben tellurido, alechols such as ethanel, Br", 1", and t" and the organic groups such as, for ellurium. Enaplice of quitable unachentate compa De ere certen noentide, earten sulfide, cartes example, ecetory, termyleny, beatoylony, etc. anderdes, and Trailing saltentite seids polytes

Suitable radical L⁶ in Formula I includes any group having in its attucture an atom with two or more unpaired electrons. Suitable groupe can contain any number of carbon atoms and hetero atoms but preferably contain is less than 30 carbon atoms and up to 10 hetero atoms selected from mitrogen, suifur, oxygen, phosphorus, areamic, selenium, antimony, tellurium, silicon, germanium, tin, and boron. Examples of such groupe are hydrocarby, groupe such as methenyl, ethenyl, propenyl, hexenyl, dodecenyl, methenyl, and carbide.

tion on exposure to energy than are salts having other anions. of the organometallic complex salts having these three anions invention that are relatively more active toward polymeriasare novel and all of these salts provide compositions of the preferably are boron, aluminum, antimony, tin, arsenic, and preferably, the anions are As76, Sbf6, and Sbf504. Some chlorine or fluorine. Illustrative of suitable anions are phosphorus. Preferably, the halogen, O. of Formula II, is as the counterien in the ionic saits of the organometallic Suitable anions, X, in Pormulas I and II, of uso complex cation to the preferred redistion-sensitive compo-GaCld, Infq, Tif6, Erfg, etc. Preferably, the anions Periodic Chart of Elements, O is a helogen atom, and r is formula DOr, wherein D is a metal from Groups IB to VIIIS are Bra", Pfg", Sbr6", Sbr5OH", Asr6", and SbCl6". Host BF4", PF6", Aef6", Sbf6", Fecl4", Sacl5", Sbf5", AlF6", metals are copper, sinc, titanium, vanadium, chromium, or a metal or metalloid from Groups IIIA to VA of the an integer having a value of 1 to 6. Preferably, the manganese, irod, cobalt, or nickel and the metalloids sitions of the invention are those in which I has the 2

Ligand 1.9 in Permula III is provided by linear and cyclic olefinic compounds formally described as having lost a hydride or a proton alpha to a double bond from a saturated carbon and heeing less than 10 carbon atoms and no beterostoms, such as for example n³-allyl, n³-butenyl, n³-pentenyl, n³-betenyl,

different any ctud from mothyl, ethyl, propyl, impropyll,

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n?-cycloheptatrienyl ligand may be formally described as an nf-carbasole, nf-biphenyl, nf-triphenylene, nf-naphthalene arometic ligand) and aromatic ligands having up to 4 rings and up to 24 carbon atoms and up to 2 heteroatoms selected being understood that both the n5-cyclopentadienyl and the nd-diphenyl amine, nd-diphenylmethane, n6-triphenylmethane re-anthracene, ne-phenanthracene, ne-pyrene, ne-chrysene, n3-namenyl, n3-decenyl, n3-cyclobutenyl, n3-cyclopentenyl, dienyl, n3-cycloheradienyl, and n7-cycloheptetrienyl (it bensens (durene), n6-pentamethylbensene, n6-hexamethylfrom nitrogen, oxygen, and sulfur, such as, for example q6-1,2,3,5-tetramethylbenzene, n6-1,2,4,5-tetramethylnl-cyclonomenyl, nl-cyclodecenyl, n5-methylcyclopentadienyl, n5-cyclopentadienyl, n5-pentamethylcyclopentaf-chlorobensene, nf-bromobensene, nf-fluorobensene, "-thiosnisole, n6-aniline, n6-M, M-dimethylaniline, n3-cyclobezenyl, n3-cyclobeptenyl, n3-cyclooctenyl, we-o-sylene, ne-p-sylene, ne-l, 3, 5-trimethylbensene mesitylenel, n6-1,2,4-trimethylbenzene, n6-1,3,5ne-toluene, ne-ethylbenzene, ne-isopropylbenzene, nf-propylbengene, n6-t-butylbengene, n6-m-xylene, triisopylbenzene, n6-1,2,3,4-tetramethylbenzene, me-cyanobenzene, ne-nitrobenzene, ne-fluorene, benrens, ne-phenol, ne-thiophenol, ne-anisole,

is eighteen. Those skilled in the art, however, hace that metallic compounds tend to be those compounds in which the sum of the electrons domated by the ligands and the metal governed by the "eighteen electron rule" less J. Chem. Md. there are exceptions to this rule and that organizatellic methoxy, ethoxy, hydroxy, nitro, chioro, brome, anthee, and involving intramolecular metal-metal bonding, this sum is 16, 811 (1969)]. This rule is sometimes called the "nine organometallic complex cations not including intramplecy orbital rule", "the effective number rule", or the "rate M.M-dimethylamino on the phenyl ring in the 2,3; 2,4; or and the valence electrons possessed by the metal, MP, MP gas rule". This rule states that the most stable organ complex compounds having a sum of 16, 17, 19, and 20 electrons are also known. Therefore, ionic salts of I, L' and L⁸ of Pormela II, and L⁹ and L¹⁰ of Pormula There are restrictions on the total aum of electrons donated by the ligands, the, the, the, the [36, 21c, 12c, 13c, 13d, 12d, 13d, 14, 15 and 16 of 1 HC, Hd, HP, and HP. For most complex compounds not 3,4 positions.

valence shell and a residual net positive charge of a ser included within the acope of the invention.

For complex scappounds described in Formula I in which intramoßacular matal-metal bending estats serious departure from the "eighteen electron rule" can occur. It has been proposed [J. Magr. Them. Soc. 100, 5303 (1878)] the departure from the "eighteen electron rule" in these transition metal complayes is due to the metal-metal interactions descabilising the metal p orbitals to an interactions descabilising the metal p orbitals to an extent to cause them to be unavailable for ligand bonding.

n12-paracyclophame, n12-1,4-diphenylbuteme, poly(n6-styreme).

poly(n0-m-vinylearbasole), poly(n6-methylphenylsiloxane),

(n6-1, 2, 1, 4, 4s, 9s)-9-(phenylmethylidens)fluorene, and

n6-quinoline, n6-tacquinoline, n6-indole, n6-benzimidazole,

metetralin, ne-ethoxybenzene, ne-benzoic acid,

me-1,2-benzopyrazole, ne-benzothiazole, ne-benzozazole,

me-indan, ne-peracyclophane, ne-1,4-diphenylbutane,

III in which complexed metal we, we, we, we sad we have

a total sum of 16, 17, 18, 19, or 20 electrons in the

metal-metal banding atts described by Formulas I, II, and

20

interactions destabilising the metal p orbitals to an extent to cause them to be unavailable for ligand bonding. Hence, rather than count electrons around each metal apparately in a metal cluster, cluster valence electron. (CVE) are counted. A dinuclear complex, when is seen to

ligands may be disubstituted by group, that may be some or

methylaming on the phenyl ring. Also, the latter two

athony, hydroxy, nitro, chloro, bromo, amino, and M.N-di-

(n6-1,2,3,4,4a,9a)-9-(3-phenyl-2-propenylidene)fluorene. The latter two ligands may be mono-substituted by groups. selected from methyl, ethyl, propyl, isopropyl, methoxy.

have 14 CVEs, a trinuclear complex, whyhe, 48 CVEs, and a butterfly, and aquare planer genmetry is seen to have 60, butterfly, and aquare planer genmetry is seen to have 60, 62, or 64 CVEs, respectively. Those shilled in the art, 62, or 64 CVEs, respectively. Those shilled in the art, compounds having a sum of 42, 44, 46, 50 CVEs for a trinuclear complex and 58 CVEs for a tetranuclear complex and 58 CVEs for a tetranuclear complex are also known. Therefore, loric salts of di, tri, or arranuclear organometallic complex cations are described tetranuclear organometallic complex cations are described by Pormula I in which the complexed metal cluster, wamb, by pormula I in which the complexed metal cluster, wamb, so or 58, 60, 67, 64 CVEs in the valence shell, respectively, and a residual net positive charge of 1, 2, or 3 are included within the scope of this invention.

guitable organometallic complax ionic salts described by Pormulas I, II, III of use in the compositions of the instantion are those acits that upon application of sufficient energy, either thermal or electromagnetic redistion having a wavelength from about 200 to 600 mm, will generate an active species capable of initiating cationic polymerisation. The level of cationic activity will, of course, depend on the choice of metal, ligands, and counterions in the salt.

Suitable fonic salts that are activated by heat to initiate cationic polymerization are those that will add an intermediate strength nucleophile such as substituted or unsubstituted trialtyl—and triarylphosphines (preferably triannylphosphines), trialtyl—and triarylphosphines (preferably pyridines, and aniliaes. Examples of such compounds are described in Tetrahedron 14, 3047 (1978) and "Carbonium ; cns" 5, Chapter 37, 1976, dilay-Interscience, Bew York. Thase reviews Contain references to the experimental procedures used to determine if a particular compound will add such a nucleophile.

Suitable ion:c salts that are activated by electricasquetic fadiation to initiate cationic polymeriza-

tion are those that upon photolysis liberate at least one coordination site on the metal. The ability to liberate at least one coordination site upon photolysis can be verified by doing a lipend exchange experiment. In such an emperiment, the compound

ligands is carbon memoxide, them infrared apectroscopy in a length, irrediation time. Make source, light source intermentalist for the particular system under study. Stamples rigorous method would involve isolation of the photograduct ment whould be carried out. A.s. organometallic tonic sait ligand concentration, choice of solvent, izradiation wave-10 indeed added or exchanged with at least one ligand Li to L⁶ spectrum before photolysis can be compared with that taken technique such as attenuntal sealysis to werify that L hos ber which the ligand exchange experiafter completion of the reaction and use of an analytion. concentration, identily of the entering ligand, entering analysis technique, etc. must be adjusted by the experiof Formula I can be determined by any number of analytical monitor the reaction before, during, and after photolysis. Ochecuten of the conditions which have been used to study ligand sity, reaction vessel, presents or absence of ouygen, 2 ligand L (L can be pt the L² or L² types). That L hes cordination sphere of the metal. If L or at least one of the List, Litt, Lid, or Li euchange reactions are contained in "Organization after completion of the reaction to determine if the is photolyzed in the presence of a potential entering determination to use some appetroacopic technique to techniques. It is particularly convenient for this suspected ligand substituted product is present. UV/visible or MAR apectroscopy can be employed. well suited technique to monitor the reaction. proper conditions a Indeed entered the 2 23 2

-20-

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references therein, and in Inorg. Chem., 19, 3007 (1960). Photochemistry", 1979, Academic Press, New York, and

complex cations useful in the composition of the invention include the following (proposed structures of typical com-Examples of suitable salts of organometallic pounds are shown at the end of the list):

(n5-cyclopentadienyl)tricarbonyliron(1+) hexafluoro-

phosphate(a).

("5-cyclopentadienyl)dicarbonylthiocarbonyliron(1+) cetrafluoroborate

2

(n2-cyclopentadienyl)carbonylbis(triphenylstibine)iron(1+) hexafluorophosphete

(n?-cyclopentadienyl)tricarbonylruthenium(1+)

(n3-cyclopentadienyl)dicarbonyltriphenylstibineiron(l+) tetrachloroferrate ?

(n3-methylcyclopentadienyl)dicarbonylnitrosylmanganese(1+) hemafluoroantimonate(b) hexafluoroantimonate

-methylcyclopentationyl) (n^3 -ellyl)dicarbonylmanganese(1+) tetrafluoroborate(C) ş

195-cyclopentadienyl)tetracarbonylmolybdenum(1+)

hexafluorophosphete

(m2-cyclobexadiemyl)tricarbonylirun(1+) hexafluoroarsenate(d) (45-pentadienyl)tricarbonyliron(1+) tetrafluoroborate (n5-cycloberodienyl)(ethylidene)carbonyltriphenyl-

(n3-cyclopentadienyl)(ethoxymethylcarbene)carbonylphosphineiron(1+) tetrafluoroborate

triphenylphosphingiron(1+) tetrafluoroborate (r5-cyclopentadienyl)(dithiomethoxycarbene)-

(1,2-cyclopentedirmyl)dicerbonylmethylisonitrileiron(l*) dicarbonyliron(1+) nexafluorophosphate

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he kaf luoroar senate

Dis (1,5-cyclopentadienyl) (1,2-ethylens) (0-methyl) tungsten(l+) nexafluorophosphate

in6-tcluene)tricarbonylmangansse(l+) hexafluoroantimonate(w)

. of -mesitylencitricarbonylrhenium(1+) hemafluorcantimonate

(n7-cycloheptatrienyl)tricarbonylchromium(l+)

hexafluorophosphate

 $(n^7$ -cycloheptatrienyl)tricarbonyltungaten(1+)hexefluoroersenate(f)

(n^5 -cyclopentadienyl) (n^2 -l-pentene) dicarbosyliron(l+)

(n6-benzene) (n3-cyclopentadienyl) iron(1+) hexafluorophosphate terrafluoroborate

(n6-mesitylene)(n5-cyclopentadienyl)iron(1+)

tetrafluoroborate

(n6-naphthalene)(n5-cyclopentadienyl)iron(1+)

hexaflucroantimonate

(n6-acetophenome)(n5-methylcyclopentadienyl)iron(1+) rsenate hexafluord

bis(n6-hexametig benzune) mickel(2+) hausfluoroantimonate bis(n6-hexameth 1benzene)cobalt(2+) benafluoroarsenate adienyl)cabelt(1+) hemafluorophosphate ladienyl)iron(1+) hexafluoroantimomate bis(n5-chlorocyglopentadienyl)nickel(l+) hexafluorop bis(n6-benzene) hrcmium(1+) hemafluoroantimonate(9) bis(n2-cyclopen bis(n^-cyclopen 2

riphenylghosphine)iridium(1+) henefluorophenylphosphinecobalt(1+) hexafluorotatracarbonyltm phosphate

tricerbonylbie(phosphate

tenyl)(macyclopentadienyl)manganese(l+) lbenzenejmengenese(1+) tetrafluoroborate rosylmolybdenum(1+) benefluorophosphate proposition (1+) tetrafluoroborate arbonylimme(1.) hemafluoroentimonate eliros(20) hexatluorosatimonete(h) e) vanadim(1+) hexafluorophosphate lum(1+) beneficoroentimonate pentecarbonylni bisin6-mesityl hexecarbonylrh (n3-ellyl)pent (n3-ellyl)tetr bising-pexament Die(no-mesity l (n'-cyclohepta 52 2

renyll(afterclopentedienyl) chromium(1.) Soaphate respete (nº-cyclooctate hexafluor heast luca

2

-cyclopest 'ienyl) iron(1+) nexalluorophosphate (1) i ne-fluorene) (1

(1,6-1-phenylborabenzene)(n5-cyclopentagrenyl)cobalt(1+) hexaf luorophosphate

-cyclopentadianyl)(n5-N-methylpyrrolyl)iron(1+)

5 (nº-2, 3, 4,5-ter: athiomethoxybensene) (n5-cyclopentadienyl)iron(1+) hexafluoroarsenate hexafluorophosphate

[(46-1,2,3,4,5,6)(n6-7,8,9,10,11,12)biphenyl]bis(n5-cyclopentadienyl)difron(2+) tetrafluoroborate

{ (46-1,2,3,4,4s,9s) (16-5,6,7,8,8s,5s) fluorene] bis(15-cyclopentadienyl)diiron(2+) hexafluorophosphate

[(n6-1,2,3,4,4a,9a)(n6-5,6,7,8,8a,5a)fluorenelbis-

(n6-benzene)ditron(4+) hezafluorophosphate

bis(n6-benzene)dichromium(2+) hexafluoroantimonate [(m6-1,2,3,4,4a,12a)(n6-7,8,9,10,10a,6a)chrysene]-

dicarbony 1 [bis (dipheny lphosphino) ethans) bis (n⁵-cyclopentatetra((n5-cyclopentadienyl)carbonyliron)(1+) hexafluorodienyl)diiron(1+) hexafluorophosphate phosphate. 7

14s,10s,18s,12s)(n6-18t,18s,18v,18v,18x,18y)-tripyrenotris [(n6-bonzene)cobalt | dicarbony | (1+) hexafluorophosphate eris(n5-cyclopentadienyl)dinickel(1+) hexafluorophosphato [(#-1,2,29,18c,18b,18a)(n6-7,8,8a,18i,18h,7a)(n6-13,14,-(2,1,10,9,0,7-defghij:2',1',10',9',8',7'-nopgret:

2-,1-,16-,9-,8-,7"-xysa,b,c.d(trinaphthalene)tetra(n⁵--4,5,5a,28c,28b,3a)(n6-8a,8b,20d,22a,22b,24c)-18,14H-4,5,6;6",5",10":4",5",6")diisoquino(2,1-a:2",1"-a¹)dipyrano(3,4,5, gh: 3',4',5'-g'h')anthra(2',1",9": cyclopentadiesyl)tetrairon(4+) hexafluoroantimonte diperimidine | bis (n5-cyclopentadieny 1) di iron (2+)

[(n6-1,2,3,36,136,136)benzo(10,11)chryseno(2,3-d)(1,3)diomolej (n5-methylcyclopentadienyl) iron(1+) hexafluoroant imonate hexafluorophosphate

acetylcyclopentadienyl)diiros(2+) tetrafluoroborale Dis(1, 2-acetylcyclopestadienyl)iros(1+) tetrafluoroborato (1,2,3,4-defs5,6,7,8-d'e's')diphenanthrenelbis(n⁵-1116-1,2,3,3a,16c,16b1116-9,10,11,11a,13c,8b)cycloocta-

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32e, 32b, 29e) naphth(0', 1', 2': 6, 5, 10) anthre(2, 3-1) naphth-(2111,3111,611,711)Indolo(2",315'6')nephth(2'3'14,5)indolo(2,3-g)naphtho(2,3-i')benso(1,2-s:4,5-s')dicar-[[n6-1,2,2,4,4a,42a](n6-16,17,18,19,19a,15a](n6-30,31,32, bazole)tris(n5-cyclopentadienyl)triiron(3+) hexa-

(n3-1,3-dimethyl-ally1)tricarbonylirom(+1) bexachloro-(n3-1-methyl-allyl)tricarbonyliron(+1) hexafluorophos

fluoroantimonate

10 [(n5-cyclopentadienyl)nichelmonacarbonyltricobalt[(+1)] hexafluorophosphate antimonate

Di-(w-carbonyltricarbonyl)(dicarbonyliros)(besacarbonylhydrodiruthenium)-w-tydro-osmium(2Fe-3u)(Fo-0e)-(20s-Ru)(Ru-Ru)(+1) hexafluorophosphate^[j] Tetra-p-hydrotetrakis[(1,2,3,4,5-m)-1,2,3,4,5-pentamothyl-2, 4-cyclopentadienyl-1-yll-tetra-tetrahedry-rhodius-(+2) bis(hexafluorophosphate)(h)

15

Bis(v-diphenylphosphido-p-carbonyl-s-methylcyclopentadienyl-

carbonyliron)rhodium(22h-Pe)(+1) hexafluorophosphate(1) Di-#-carbonylpentacarbonyl-w-carbonyldi-W-cyclopentadienyldirhodio)ditron(fe-fe)(4fe-fh)(fb-fh)(+1) hexafluoroersenate(B) 20

Di-#3-carbonyltricarbonylbis(*-cyclopentadienylmichelio)iron(2fe-Hi)(Ni-Hi)(+1) banafluoroantimonata(n)

1

The state of the s

where X is -0- or -HR"-- (where R" is hydrogen or lower

alkyll, R' is hydrocarbyl, hydrocarbylcarbonyl, helosydrocarbyl, or hydroxyhydrocarbyl when x is oxygen, or R' is hydrocarbyl, hydrocarbylcarbonyl, or hydrocarbylaulfonyl other hydrocarbyl, or R. (as hydrocarbylcarbonyl) and R. when X is nitrogen, and Y is hydrogen, alkyl, aryl, or , cucture containing nitrogen as a betero ring atom. can be c ... sected to form a 5- or 6-membered cyclic

alkaryl, arylalkyl, and the like. In general, mondmers of this type contain a tinyl group and are typicied by theyl ether, vinyl arbutyl ether, vinyl 2-chloroethyl ether, alkyl ethers, such as vinyl methyl ether, vinyl ethyl men alkyl, altenyl, eryl, cycloalkyl, cycloaltenyl, term "hydrocarbyl" is used herein in its useal sense vinyl isobutyl ether, vinyl phospi ether and vinyl

of from 1 to 6. preferably 1 to 3. Perticularly upoful and

the alignments, eyclosliphents, and glycidyl other type

respected and will typically have an aport aquivalency

my can be allighette, cyclosliphetic, arometic, or

echains ago the sea

meric and polymeric types of sporides

segen, march bather, Inc. (1969). Suitable 1,2-cyclic

maing Polymeriastions", Vol. 2, by Princh and

a. plyciagi other of bisphenel A. J. 4-eponycyclobenyleethyl

nescarbonylate, 3,4-spony-6-methylcyclo-

any leachyl-1, 4-apany-6-methyleyelohezaneesthonylete.

al che

eng - 6-mothy leye lobery lasthy 1) ad spets,

17.73

Houses, glycidal, butadione oxide, glycidyl methocrylate,

styress exist, visyleyclobeness oxide, visyleyclobeness

1.3-sportes such as propylene oxide, epichlorohydrin,

2

octamesulfommide and H-vinylpyrrolidone. A description of butyl ether, and H-vinyl compounds such as H-vinyl-H-me'hyl winyl monomers and their use in propering polymers is set 2-ethylhesyl other, vingl ethers of substituted aliphatic alcohols such as 1,4-di(ethenoxy)batene, vinyl 4-hydroxyforth in "Vinyl and Related Polymers." by Schildknecht. published by John Wiley's Sons, Inc., New York (1952). 2

Other cationigally-semaitive monomers which can be polymerized in this invention include ethylenically unsakurated hydrocarbons such as isobutylens, 1,3-buka-2-vingl-1,3-dioxolane and 2-methad-1,3-dioxolane: and diese, incpreme, styress, and diwinglbenremes cyclic formals such as trioxams, 1,3-diesolane.

thesthylationses hering cyclosliphetic epoxide or glycidyl

, e-buresettol digipcidy other, polyglycidy, other of

mendieme atomide, aponidined polybutedieme,

malfactualdehydo reseals or sevolek reals, resorciael

digiyetdyl other, and opcay allicones. e.g.,

ther groups. A other meriaty of commercial openy resina

and Seville, define Mill Sect Company, See Seck (1967)

to "thuny flects technology" by P. F. Bruine, John

omiliate and listed to Tenthert of theny Bests. by

Aspessmenterine of the 1.3

course which can be polymerized in eccordance with this

savention to copresented by the general formulas

Another angles class of cationically-sensitive

3,3-bis(chlocomothy)leasters, and tetrahydrofurms.

and 1,4-cyclic others which can be polymerized in

Miley 6 Sces, May Nest (1966).

accordance with this impation are castame.

redical, a garboxy-containing hydrocarbon redical or ester cyclic silosanes which can contain various groups attached group, a cyanobydrocarbon radicate, hydrogen, halogen or a to the silicon atom such as a hydrocarbon radical (alayl, allyl or acryloyloxy-albyl), a halogenated hydrocarbon aryl, elharyll, an elhenyl nydromerbon reducal (vinyl. hydrony group. Representative opelic siloxanes are 2

ethylemically emmanated hydrocarbons, cyclic formuls, and

1,3-, and 1,4-epoutdes), vinyl others, B-vinyl compounds

-52-

cyclic organosilomnes. An extensive list of cationically

polymerizable manages which can be used in this invention

220 given in U.S. Detect Bos. 3,347,676 and 3,842,019.

see with this amention include those described in

The cyclic ethers which can be polymerized in

the processes of relatively low molecular weight linear ediaments out as became thy low molecular weight linear distances out as became thy linears, chloropentamethyldislinears, chloropentamethyldislinears which serve to commisse the growing chain and provide stable fluids or claids having practive and groups.

gipcol (e.g., "gill-1850" and "ERL-1952"), dipentene dionide estion. In perticular, cyclic others which are readily patientcally-semaitive monomers which can be used in this may's placingl other. 1,3-button onide, diglycidyl other -car-assors, estiments epocy meditied with polypropylems and & to.g., "then 630" and "Off. 331"), winglmes dienide (e.g., "ER,-426"), 3,4-sponyeyelo-.th. glycifid, glycidyl methecrylate, octylene oxide, dries, contrabplicationes, express caide, viewlayelabones estable tembrie progrismo onide, ometane, epichlorosis(1,4-quay-C-nethylepelchenylaethylledipate (e.g., Ph.-4221'), 3,4-spory-6-metayleyeloheayli sthyl 3,4-Thore to a host of comercially available mycyclobezamecarbonylate (e.g., 6-methy legelsthemanacathasylate (e.g., "fitt-4201"), Vancturi-Lat

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"Epi-Rez 5/1" and "DEN-418"), resorcinol diulycidyl ether (e.g., "Ropoxite"), polyglycol diepoxide (e.g., "DER 736"), polygcrylate epoxide (e.g., "Epocryl U-14"), urethane modified epoxide (e.g., "QE3599"), polyfunctional flexible epoxides (e.g., "Flexibiliser 151"), and mixtures thereof

spoxides (e.g., "Flexibiliser 131"), and mixtures thereof with co-curatives, curing agents, or hardeners which also are well known (see Lee and Meville and Bruins, supral. Representative of the co-curatives of hardeners which can be used are acid anhydrides arives of hardeners which can be used are acid anhydrides. On suc. as madic methyl anhydride, cyclopentanetetracerboxylic dianhydride, pyromellitic anhydride, cis-1,2-cyclo-hexanedicarboxylic anhydride, and mixtures thereof.

in general, the polymerisation of cationically—sensitive monomers with the lonic selt of an organometallic complex can be carried out at room temperature for the majority of cationically—sensitive monomers, although low temperature (e.g., -10°C) or elevated temperatures (e.g., 10°C) or elevated temperature (e.g., 10°C) or elevated temp

2

range of 50° to 250°C, preferably from 50° to 150°C, can be monomer (1.4., & catalytically effective amount) under the accelerate the polymerization. In the case of latent salt Much amount generally will be in used as a catalyst in this invention should be sufficient catalysts of this invention, temperatures generally in th. the range of about 0.01 to 20 weight percent, preferably organometallic complex to be to effect polymerization of the cathonically-sensitive used. The temperature of polymerization and amount of spendent on the particular application of the polymerhed or cured product. The ser used and the desired catalyst will wary and be cationically-sensitive mos amount of ionic salt of a desired use conditions. 25

sensitive monomer.

Solvents can be madd to assist in dissolution of the sonic salt in the cationically-sensitive material and

0.5 to 5.0 weight percents and most preferably 1.0 to 2.0

weight percent, based on the weight of cattonically-

(e.g., 'gr. 1169'), apoxidized polybutediens (e.g., 'Guiron 261'), silicana apoxy (e.g., 'Syl-Kam 90'), 1,4-butenediol

diglycidyl other (e.g., "Arabbite MD-2"), polyglycidyl

server of phesoudormaldshyde sovolat (e.g., "DER-431",

-20-

Are preferred for use in the polymerisable compositions.
Representative solvents include acetone, methyl ethyl
ketone, cyclopentonome, methyl cellosol's sostate,
methylass chloride, mitromothene, methylformets,
acetoaltrile, and 1,2-dimethonyethene (glyme).

The cureble or polymerisable compositions of this invention congrising the outsideally-mentitive monomerial and the ionic selt of an organizability complex as catalyst can be used for applications such as those in which other certamically-mentitive organizations amploying levis acid certamically-mentitive organizations amploying levis acid certamically-mentitive orders or district arbitration mentities online salts are used. Thus, the ommostions on me mentity orders candidan composition of constant and modified compositing and sealing organizating compositing and conting compositing attricts.

espending on the particular cationically-sensitive monomer and tenic expensatallic complex used. In addition, the composition may cantain adjuvants (e.g., filliers, such as silica, tale, also subbles, clay, reinforcing fibris, dyes, planeste, planticiants, also espents, anticulants, surface addition agents, anticulants, surface attents agents, etc.,) as long as they do mat interferents the polymerization of the cationically-symplities composition or, where the issic salt of the composition or, where the issic salt of the composition to which the complex is responsive.

For those compositions of the immedian which are cationically—consistions end an ionic sait of an exponential complex of formulas I, II, and IIII, any compared and visible society radiation include account of section of the apostrum (e.g., about include account where discharge lamps, carbon account of unposition lamps, publight, etc. The required account of unposition to effect polymerization is dependent upon such factors as the identity and concentration of .ne organization controller fonts complex, the particular cationically—

(1973), and include pyrane, fluoroanthrene, benzil, chrysene range of 6.01 to 10 parts, and preferably 6.1 to 1.0 parts, Any photosensitizer may be useful if its triplet energy is Handbook of Photochemistry, Marcel Dekher Inc., My, 27-35 p-terphesyl, acenerathene, rephthelene, phenenthrene, and bighenyl. When present, the amount of sensitizer used in the practice of the present invention is generally in the Optionally, by weight of sensitiser per part of organometallic salt. sensitive monomer, the thickness of the exposed meterial, type of substrate, intensity of the radiation source and it is within the scape of this invention to include spectral sensitizers in the radiation-sensitive composition. at least 45 kcal/mole. Examples of such sensitizers are given in Table 2-1 of the reference, Steven L. Murov, amount of heat associated with the radiation.

The objects and advantages of this invention are further illustrated by the following examples, many of which utilise as cationically-sensitive moment a stock solution ponsisting of 1 part by weight of vinylcyclobeaned dioxide and 1 part by weight of vinylcyclobeaned dioxide and 1 part by weight of 1,4-sponycyclobeaylmethyland amounts thereof sectod in these examples, which are in parts by weight, as well as other conditions and details should not be construed to unduly limit this invention.

EXAMPLES 1-4.

ं **इ**ट Polymerizable solutions were prepared by mixing in four switchle vessels 10 parts of stock solution, 1.0 part of scennitrile, and 0.1 part in each vessel respectively, of Enample 1) the hexafluoroantismeste, (Enample 2) the hexafluoroantismeste, (Enample 3) the hexafluoroantismeste, end (Enample 4) the tetrafluoroborate salt of ("6-mesitylene)("8-cyclopentadienyl)iron(10) (each prepared as described in W. A. Hendrickson, Ph.D. thesis, U. of Florida (1978)). The solutions were coated onto polyvinylidess chloride primed 75 micrometer polyester using a number 22 wire wound coating rod and the coatings allowed

duce a non-tacky surface for each sample is given in Table I. 10 cm from the sample surface. The time required to proexposed to a 150 watt tungsten opothight at a distance of to air dry for 10 minutes. The coated samples were then

TABLE 1

Time to produce non-tacky	120 Ben
1eny1)-	
Counterion of (n6-mesitylene)(n5-cyclopentadienyl)-	
Counterion of ne)(n ⁵ -cyclopen iron(1+)	200 P
mosity).	
Ex. (ne	7 8 8 4

(a) becomes non-tacky after heating at 100°C for 60 min.

EXAMPLES 5-7

dienyl]iron(1+), end (Example 7) (n⁶-pyrene)(n⁵-cyclopentedescribed in Examples 1-4 and other samples of the coetings Coatings were propared as described in Examples Fespectively, (Example 5) (n 6-naphthalene)(n 5-cyclogentadienylliron(1+), (Example 6) (n6-chrysene)(n5-cyclopentadienyl)iron(1+). (These salts were prepared according to produce a non-tacky coating for each sample is recorded in 1-4 using as catalyst the hexafluorophosphate salts of the procedure described in 3. Organometal, Chem. 101, 221 (labeled (c)) were exposed to the output of the 150 wate removed 998 of the radiation below 440 nm. The time to exposed to the output of the 150 watt tungsten lamp as tungsten lamp that passed through a light filter that (1975)). Samples of each coating (labeled (b)) were

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Time to produce

	Catalyst	<u>@</u>	(8)
No. Dexact.		no filter	no filter Asses sites
jeu-9u)	(ne-naphtha: ne)(n5-cyclo-		*****
Pent	. :	2 2	3
(ne-ch	(n ⁶ -chrysene)(n ⁵ -cyclopente.		
diem	dienyl)iron(1+)	30 8ec	9
(n ⁶ -pyr	(n ⁶ -pyrene)(n ⁵ -cyclonente-		
dieny	dlenyl)iron(1+)	15 sec	9 9 9

EXAMPLES & and 9

as catalyst the hexafluorophosphata salt and the banafluoro-The time required to produce a non-tacky surface With the hexafluorcantimenate salt, exposures to produce a The procedure of Example 5-7 was repeated using with the hexafiuorophotehate salt was 60 seconds for expesures without the filter and 120 seconds with the filter. The $(n^6 - \ell 1 \text{ Lorende}) (n^5 - \text{cyclopentadiengl}) \text{ Area}(1+)$ antimonate sait of (n6-flaorene) (n2-cyclopentadicay))non-tacky surface were 10 and 60 seconds respectively. 1ron(1+).

saits were propered as described in Mendrickson, Ph.D. thesis, Univ. of Florida (1978).

EXAMPLES 10-15

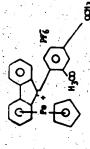
Table III. Each solution was coated and dried as described parts of stock solution, 2 parts of ecetons and 6.1 part of each of the various organisatellis complex salts shown in in Examples 1-4 and exposed as described in Examples 5-7, The time required to produce a non-tacky autiage for each Coating solutions were proposed by mining 10 is given in Table III.

Time to produce non-

	j <u>s</u>		tacky auriece sec.
	il :	Catalyst (0), (0)	ne filler 440m filter
^	2	(10-1, 2, 3, 4, 4s, 8s) -9-(4-mathy labory 1-	
	. *	methylidene)fluoreme)-	
,	:	(12-c)clapentedien; 1) iron(1+)	2
	· =	1m6-1,2,3,4,4,4,90)-4-14	
٠		Phery Lestly Liders £ Lucrens -	
		(1) Syclopentadieny) (ren(1+)	15
	77	(106-1,2,1,4,46,90)-9-(2,4-dimethony-	
	٠.	phery lawthy 1 idens) fluorens]-	

13 (m ⁶ -1,2,3,4,4a,9a)-9-(3,4-disschony-pharylaschylidens)(liceruns)- (m ² -cyclopentadisryl)iron(l*) (*) 15	pheny Lestry 1 idena) f lucrema] - (n ² -cyclopentud lany 1) iron [1+) 30	ethony (*)
	13 {m ⁶ -1,2,3,4,4a,9a}- 9 -(3,4-dimethony- pharylmetrylidene){lincrone}- (**-cyclopentadienyl)iron(1+) (*)	
	13 [m ⁶ -1,2,3,4,4a,9a)-9-(3,4-dissebory- pharylastylidens)[licerons]- (1 ³ -cyclometedian)[licerons]	

120



EXAMPLE 16

Ph.D. Thesis of W. A. Mendrichson), was coated and dried as A coating solution, prepared by mixing 10 parts of stock solution, I part of acetomitrile and 0.1 part of phosphate, (prepared as described in the previously cited seconds were required to produce a mon-tacky sunface when the coating was exposed to the output of a 275 watt G.E. non-tacky surface was obtained in 60 seconds. Only 30 (n6-toluene)(n3-cyclopestadienyl)iron(1+) hexallu-ro-10 described in Examples 1-4. On exposure of the dried coating to a 150 watt tungsten spotlight at 10 cm, a 15 sunlamp at 10 cm.

EXAMPLES 17 AND 18

 $(n^6$ -styrene) \sharp ricarbonylmanganese(1+) hexaflugrosreenete in (n3-cyclopendadienyl)iron(1+) hezafluorophosphate or polysple 16 was repeated using poly(nd-styrens)-Sphate. Exposure time were 120 seconds and 45 seconds up produce a non-tacky coating using the 150 place of (necoluene) (n5-cyclopeatedienyl)iroa(1+) watt rungste spotlight and the 279 watt sunlamp hexafluoroph respectively

described in the before-mentioned Ma.U. thesis and the polyhaving a number average molecular weight of 22,000 in place of mesityless or toluene, respectively. The iron complex J. Cl.en. Sog. (chem. Come.) 688 (1873) using palyatyrene The polystytene from complex was prepared as styrene manifemene complex was prepared as described in 2

⁴⁻methy | Denzal denyde, 4-methoxybenzal denyde, 2,4-dissthoxybenzal-Cuenylliscon(1+) hexaflucrophasphase (propared in Example 8) using Dehyde. 3,4-dumethoxytonzaldehyde, cinnamaldehyde, and 4-8,N-di-Prepared by first condensing the corresponding aldebyde (i.e., a catalytic amount of potassium hydroxide in aquadus ethanol mechylaminocentaldehyda) with (n⁶-fluorene)(n⁵-cyclopenta-(d) All counterions are herafluorophosphate ister nitragen. ٤

EXMPLES 19-51

Polymerisable solutions were prepared as described in previous examples using the polymerizable compositions and the organometallic salts listed in Table IV. Each solution was coated onto primed polyester film and the coating dried as previously described, and exposed to polymerizing conditions as shown in Table IV. The time required to obtain a tack-free coating for each is given in Table IV.

9

2

Interpretation of the state of

hexacl uncount amonate/hydroxypantafluoro- 10 sec

(k)bis(n6-haxamethylbanzane)cobalt(2+)

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4 P. V. W. C.

-38- That IV continued organization complex salt(f) organization(le) terrathoro- relatiblesison(le) terrathoro- gra	borate (*) nameCartory Intention(!*) hexa- £luconent imcrete/hydronypambeflucro- 20 sec antimonate (*) (*) (***-cyclonent add say) inflantion**-		15 (7) (1) (n ² -mathylogologamtadiamyl)dicar- bonylaitronylmangamana(1+) hamafluozo- antimonato antimonato (1+) hamafluozommanato (1+) hamafluozommanato (1+) hamafluozommanato (1+) hamafluozommanato	20 (9) (u) (n ⁶ -consens) (n ² -cyclopmizationyl) (son (1+) hass (lucroscenate 15 sec 50 (u) (n ⁶ -cortenate) fi ⁵ -cyclopentationyl) (son (1+) hassilvorophospheta	25 (1+) heartlucrees terms 25 (1+) heartlucrees
: a	15 (0) (n°—maitylens) tricactionylithenium(1+) Menafluctuarisenste 15 (F) (n²—cyclopentuallanyl)dicactionyl— Grighenyliphaghinelith(1+) Grighenyliphaghinelith(1+) 10 hemafluctuarishate 240 esc	## (F) ft %_opelgentation(1) dicartony1- ####################################	triptery integration (1+) *** ** ** ** ** ** ** ** **	Hary Idicartomy - cos (1+) to tieny Idicartomy - ton(1+)	(r)(n ² -cyclopertediany))dicetonyl- (r)(n ³ -cyclopertediany)dicetonyl- (r)(n ³ -cycl

ies 22 and 51 in which 2 parts of nitromethans stooglate, and I part of ecotonitrile with me dioxido, 5 parte of 3,4-spongayclohenylaethylples 19-21 is which 2 parts of scetonitrile art of the lonic complex in a mixture of 5 parts of Contings were sade as described in previous emploe using by AL BIT

the uning a 275 wett G. E. mailump at a distance of 16 on from the conting.

ace with the procedure outling

ENLIS Che. 186, 265 (1980).

J. One. for. (Ope. Ope.) 500 (1971). 2 4 11 15 (1944),

de Brath, 6, 112 (1960). 3

2. Summerlik Om, 13, 10 (1969).

P. Ptc. (Orn. Orn.) 311 (1941). 12 Sto (1968).

Br. Cres. S. 1037 (1966).

Se. (One. One.) 64 (1975). Om L 83 (1962).

1956 Com. J. 165 (1955) and Latter, See, S. 1177 (1966). 3

mentile dentemble. A. R. S. King, Amounte Press, M.Y. 1965. 2. th. Chim. Sec. 29, 478 (1977).

mirrichade, M.A. thanks, U. of Floride (1978). H. Che. Ital. 68, 1170 (1950).

EXAMPLES 52-63

cetalyzing the polymorization of cationically polymerizable of sonic selt as shown in Table V. Lech misture wes coated percent by weight, based on total weight of stock solution, compounds, solutions were propered as described previously unto polytvanyladene chloride) primed polyeeter sheeting, oried, and exposed to the radiation of a 275 watt G. E. consisting of stock neletion, solvest, and 10.0 to 0.01 toute saits of organometallic completes effective for To illustrate the reage of concentrations of 30

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non-tacky to the touch. The results are given is Table V. sunlamp at a distance of lo ca until the costing was

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Lonic occumentallic complex sait bis(n^-maity)ems)icon(2*) hemaflucco entimonate bis(n^-maity)ems)icon(2*) hemaflucco entimonate bis(n^-maity)ems)icon(2*) hemaflucco entimonate bis(n^-maity)ems)icon(2*) hemaflucco entimonate (n^-cyclopentallenyl)dicartonyl- erit/ordyletiblenicon(1*) hemaflucco entimonate (n^-cyclopentallenyl)dicartonyl- trip'oryletiblenicon(1*) hemaflucco	Corc. of The of	l	1.0	0.01 20 min 10.0 5 mc	•	0.1 45 Bec
Ignic creaters Themsityless)11 Themsit	Milc orplar salt	con(2+) herafluceo-	on(2+) hearfluoro	dicertory)	it) beationyl- it) beativoro- licertoryl-	* handluoro- icarbary.
	Ignic organisate	bio(17-mesity)ime)); entimonate	bie("-meity)lame)ir entimonate bie("-meity]lame)ir entimonate		erichmylatibishirmil erichmylatibishirmil erichmita (n ² -cyclopenessiony))	antironte (n3-cyclopentaliany))d Effice yastinima ron()

in Grantly lead in S-cyclo-

Jentadionyl) iren(1+) hexafluoroant unou...

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differe departing from the morpe and opinit of this immedian, and it should be understood that this invention to make to be underly limited to the illustrative embedians:

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CLAIMS

THE RESERVE

prising a cationically polymerisable composition comcatalytically effective amount of an ionic salt of an organometallic complex cation capable of adding an intermediate attength mucleophile or upon photolysis capable of liberating at least one coordination site, said metal in said organometallic complex cation being selected from elements of Periodic Groups IVB, VIB, VIB, and VIIB. 2. The compesition according to Claim 1 wherein amid ionic salt has a formula selected from Pormulas I, II, and III:

ī

[(L¹a)(L²a)(L³a)_Ma)_G((L¹a)(L²a)(L³a)_Ma)_h-[(L¹a)(L²c)(B³c)_Ma)_J((L¹a)(L²a)(L³a)_Ma)_h- wherein Me, Mb, Mc, and MG each represents a metal selected from the elements of Periodic Groups IVE, VE, VIE, VIE,

Lis, List, List and List such represents none or 1 to 6 ligands contributing an even number of d-electrons

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The state of the s

41-. and tel-dentate ligand., each contributing 2, 4, that can be the same or different selected from sonoor 6 e-electrons to the valence shall of Ma, Mb, NC, and of preparetraly,

LPD, LPE, and LM each represents note, 1 or 2 ligands sentributing one e-electron each to the valence shell of are, urb, ap, and ad respectively,

-electrons to the valence shells of two or more metal s-elections that can be the same or different ligand cassata acao or 1 to 6 bridging ligands containing saleoted from embetituied and unsubstituted acyclic somegelic endetic compounds; sech capable of nd cyclic unseturated compounds and groups and oting as a bridging ligand contributing 2 to 24 toms and, and, are and simultensously:

ments came or 1 to 12 bridging lipsade contributing an even amang of e-clectrons that can be the same or ligands, each deserted 2, 4, or 6 a-cleatross to the malesco aballa ef two or more metal atoms Hª, Hb, Ho, different enlected from mono, di, and tri-dentate or of stanteneously;

with the provide that the total electronic charge contributed Sents sens or 1 to 12 bridging ligands contributing 1. 2. le er d e-alectrons to the valence shalls of two or mace metal atoms me, atb, we, or we atmultaneously: the man of londe charge on me, mb, me, and me results in a to and, and, and and any the lifeste Lite, Lite, Lite, 116, encident act penitive change of a to the complex.

o do es incipor baying a usino of 1, 2, or 1, the residual electrical aborgs of the complex cations

K is a helogal containing complex anion of a metal or metal laddy

f is an integer of 1 to 3, the sumber of complex anions requires to apetralise the charge e on the complex Cation, and

9. B. J. and & ladependently are 0 or 1, with at least one

0109851 of them being equal to 1;

3x0+ [ax(01)(71)]

where in

contributing two to twelve s-electrons to the velence eslected from substituted and unsubstituted edyclic and alloyello unesturated compounds and groups and L' represents none, one, or two relectron contributing ligands that can be the same or different ligand heterocyclic aromatic compounds, each capable of We represents a metal selected from elements of the Periodic Groups IVB, VB, VIB, VIIB, and VIIIB; substituted and unsubstituted carbocyclic and shall of MP,

provise that the total electronic charge contrirepresents nows of 1 to 6 Mgands that one he the age or filterent ligand selected from mono-, di-, and dentate ligands, each contributing 2, 4, or 6 A residual net positive charge of a to the buted to Ha by L' and L' plus the lonic charge on Me Octrone to the valence shell of MP; recults

or K and f are as defined above; and

((L9) (L10) MP1 *9rn

Matte a metal selected from Cr. No. W. Mn. Da. Po. 8 20 Proper de where in

that can be the same or different ligand selected from L9 represents one oritio --electron contributing ligands **-aromatic compounds selected from 16-bensene and 45-myolopentadiemyl, and a7-cyclohaptatrienyl and substituted and unsubstituted a l-allyl,

supptituted ne-bensene compounds and compounds having # fused rings each capable of contributing 1 to "electrons to the valence shell of MP;

0109851 Lie represents none, 1 to 1de contributing two

with the provide that the total electronic charge O-clectrons to the valence shell of MP;

We en all greatles in a residual not positive charge of q contributed to up by ligands L' and L'lo, plue the lonic a the employe

E is an integer baying a value of 1 or 2, the residual

T is a bologen containing complex anion selected from electrical charge of the complex cations

a is an integer of 1 or 2, the number of complex anions re-AMOU. Biff. and 207,00-, and

quired to sectralise the charge q on the couples cation.

1. The amposition according to claim 2 wherein is December 1, the ligands Lie, Lib, Lie, and Lid of the

each emitains less than 100 carbon atoms and up to 10 becare atoms melected from nitrogen, sulfur, carpen, phospherus, ermeale, solenium, antimony, tellurium, sillions, Garmanian, tin, and borons

the Massats 122, 128, 126, and 126 of the louis salt such

ittenic, selenius, antique, tellurius, and digitation ligands capable of forming with entitlements and and and to 10 carbon to ederapes, sulfur, cayoes, phosphorus, Persons, soldenies, sectonsy, tellurius, in America my to 10 bototo atoms solected late sitzages, aulius, cayoes, pheephorus, otems and up to 18 hotero atoms delected functioned seturated or unacturated ring ment set, and, and, or and or e., tr, or difficien to the metal neum,

the Manues (No. 178, 178, and 178 of the louis salt each has up to 10 certain grams and up to 10 hotors ocus

0109851 selected from nitrogen, sulfur, omygen, phosphorus, ersenic, selenium, antimony, tellurium, silicon, Vermentum, tin, and borons

the bridging ligand L4 of the ionic salt contains less than 100 carbon atoms and up to 10 betero atoms selected from nitrogen, swifur, oxygen and nitrogen, sulfur, oxygen, phosphorus, ersenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron;

the bridging ligand L⁵ of the lonic salt contains up to 30 Carbon atoms and up to 10 betero atoms selected from nitrogen, sulfur, oxygen, ghosphorus, ermenic, selenium, antimony, tellurium, and borom; and

carbon atoms and up to 10 hetero atoms melected from selenium, antimomy, tellurium, ellicom, germanium, bridging redicel L6 of the lonic sait has up to 10 nitrogen, sulfur, oxygen, phosphorus, armenic, tin, and boron; 3

wherein, in formula II

20

Carbon atome and up to 10 betero atoms selected from nitrogen, sulfur, oxygen, mitrogen, selfer, oxygen, Phosphorus, areasic, selenium, antimose, tellurium, ligand L7 of the ionic salt contains less than 100 siliann, germanium, tin, and boron;

ligand L⁰ of the lonic salt is selected from

amtimony, tellution, ellicon. germanium, tin, and monodentate ligands having up to 38 carbon atoms and up to 2 betero atoms selected from nitrogen, selfur, oxygen, phosphyrus, arsenie, selenius, Moron, and

unsaturated ging containing up to 10 hetero atons polydentate ligands capable of forming with metal Me de, Se, or 6-mambered saturated or

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tellurium, ellicon, germentum, tin, and borom in prosphorus, arsenic, selenius, antimony, selected from nitrogen, sulfur, ouygen, addition to the metal atom; and

wherete, is Permits III

ligand L¹⁰ of the ionic sait is selected from carbon ligand L⁹ of the ionic salt contains up to 24 carbon and up to two heterostoms selected form nitrogen, memorish and the mitroscolum ion, and and milfur. Decyons.

2

The composition according to claims 2 and 3 Mydrocarbylcarbonyl, Mydrocarbylcarbonamido, phamyl, amo, aultur, omygen, phonphorus, ersenic, selenius, astimony atoms and up to 10 betero atoms selected from nitrogen, dimeth_lamino, diphenylphosphino, trimethylsilony, and condessed rings, said group containing up to 30 carbon independently unsubstituted or substituted by a group wherein the ligands Lle, Llb, Llc, and Lld each is tellurium, ellicon, germenium, tin, and boron, and boryl, halo, hydromy, cyano, nitro, nitroso, omo, hydrocarby lastcapto, hydrocarby losycarbonyl, melected from hydrocarbyl, bydrocarbyloxy,

hydrocarbylcarbomyl, bydrocarbylcarbonamido, phenyl, aso, aultur, omygen, phosphorus, arsenic, selenius, antisony, atoms and up to 10 metero atoms selected from nitrogen, disetbylasino, diphonylphosphino, trimethylsilouy, and condensed rings, said group containing up to 30 carbon wherein the ligand L7 or L9 is substituted by a group boryl, halo, bydrowy, cyano, nitro, nitroso, ouc, selected from hydrocarbyl, hydrocarbylosy, tellurium, milicon, permentum, tin, and boron, hydrocarbylmercapto, bydrocarbylomycarbonyl,

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ethylenically-unseturated hydroserbons, eyells formals, and merein seid polymerismis - eterial is melected from The composition according to any preceding lic others (also designated as 1,2-, 1,3-, and group sentaining meterial, 1,3- 1,3-, and 1,0-offices), viryl others, k-vinyl ompound sycile organosilomenes.

The composition according to any presental claim wherean said sait is present in an amount in the range led 0.01 to 20 weight percent of soid cationisally Polymerisable meterial. .

2

claim further comprising in the range of 0.01 to 10 parts 7. The composition according to any prescoting by weight of a spectral sensitizer per part of stallic salt.

where the sale sale, sal 8. The composition according to claims 2 to 7 LBb, LBc, L3d, L4, L5, and L4 liqueds independently are Oroupejon a polymeric chain.

to any proceeding claim, sold gresses emprishing schiulng said entionisally polymerisable meterial with a catalytically affective mount of eals tonic salt of an organs A process for palymentaing the commetallic complex, and

2

cuelds the resulting admixture with a the or estinic reduction course, 10. A compound according to Claims 2 to 7 having the formula:

[(L9)(L10)NP) +qxn

wherein

MP represents a metal selected from Cr. No. W. Mn. Re. Pe. 8

Lo represents 1 or 2 ligands contributing s-electrons that eubstituted of bensene compounds and compounds having substituted and unsubstituted n3-silyl, n5-cyclopents 46-arcmatic compounds selected from 46-bensene and can be the same or different ligand selected from dienyl, and n?-cycloheptatrienyl and substituted

2 to 4 fused rings each capable of contributing 3 to represents none or 1 to 3 ligands contributing an ev 12 s-electrons to the valence shall of MP;

different ligand selected from carbon monoxide or number of e-electrons that can be the same or altrosonius

buted to MP by L9 and L10 plus the lonic charge on matel MP with the proviso that the total electronic charge contriresults in a net residual positive charge of q to the ons-

@ is an integer having a value of 1 or 2, the residual electrical charge of the complex cation;

I is a halogen-containing complex anion selected from Aef6", Sbr6" and SbrsOHT; and

complex anions required to neutralize the charge q on a is an integer having a value of 1 or 2, the number of the complex cation.